CHEMISTRY 225 2000-01

SECTION A: Multiple Choice [1 mark each = 32 marks]

Use the following information where appropriate:
$R = 8.31\ J\ mol^{-1}\ K^{-1} = 0.082\ atm\ dm^3\ mol^{-1}\ K^{-1}$
$K_w = 1x10^{-14}$

Each question is followed by five suggested answers. Select the best answer and shade the letter corresponding to this answer on the answer sheet provided.

1. The table shows data for the reaction $A + 2B \rightarrow 2C$ at constant temperature.

Initial [A]/M	Initial [B]/M	Initial reaction rate/Ms^{-1}
0.10	0.10	$2.53x10^{-5}$
0.10	0.20	$5.06x10^{-5}$
0.30	0.10	$22.8x10^{-5}$

The rate law for the reaction is

A $R = k\ [A]^2[B]$
B $R = k\ [A]^2[B]^2$
C $R = k\ [A]\ [B]^2$
D $R = k\ [A][B]$
E $R = k\ [A]2[B]$

2. The reaction $2ClO_2(aq) + 2OH^-(aq) \rightarrow H_2O(l) + ClO_2^-(aq) + ClO_3^-(aq)$ is first order in hydroxide ions and second order in chlorine dioxide. The rate of formation of the chlorate(V) ion in a particular experiment was 0.016 Ms^{-1}. What would be the rate of formation of this ion, in Ms^{-1}, if the concentration of hydroxide is quadrupled and that of chlorine dioxide is halved?

A 0.002
B 0.004
C 0.064
D 0.032
E 0.016

3. The following mechanism has been proposed for a reaction.
Step (a) $NO(g) + Br_2(g) \rightleftharpoons NOBr(g) + Br(g)$ fast
Step (b) $NO(g) + Br(g) \rightarrow NOBr(g)$ slow

Which statement is **NOT** consistent with this proposed mechanism?

A The overall reaction is $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$
B Br is a reaction intermediate.
C The reaction second order.
D The energy of activation for step (a) is lower than that for step (b).
E The rate law for the reaction is $R = k[NO]^2[Br_2]$

4. At 298K, K_c for the process $Si(s) + O_2(g) \rightleftharpoons SiO_2(s)$ is $2x10^{142}$.
Which **CANNOT** be deduced from the data?

A $K_c = 1/[O_2]$
B The $[O_2]$ in any equilibrium mixture of silicon, oxygen and silicon dioxide at 298K is $5x10^{-143}$ M.
C When silicon and oxygen react, the limiting reagent is almost completely used up.
D When silicon and oxygen are mixed, they immediately react to form SiO_2.
E K_c for the reverse process is $5x10^{-143}$.

5. The equilibrium constant for the reaction $X(s) + Y(aq) \rightleftharpoons Z(aq)$ is 2.4×10^{-6}.
Which of the following statements is **TRUE**?

A The equilibrium concentration of Z is less than that of Y.
B Adding some more X will increase the equilibrium concentration of Z.
C Adding a suitable catalyst will increase the equilibrium concentration of Z.
D Adding a suitable catalyst will increase the value of the equilibrium constant.
E Adding more Y will increase the value of the equilibrium constant.

6. At 1000K the equilibrium constant, K_c, for the reaction
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 2.8×10^2.
Five systems were set up with initial concentration of each gas as shown in the table. In which system will the **reverse** reaction occur to establish equilibrium?

	$[SO_2]$/moldm^{-3}	$[O_2]$/moldm^{-3}	$[SO_3]$/moldm^{-3}
A	0.02	0.03	0.04
B	0.02	0.02	0.08
C	0.04	0.06	0.08
D	0.04	0.02	0.08
E	0.02	0.15	0.04

7. At a given temperature, T, some $COCl_2$, at an initial concentration of 0.10 M, was placed in a container and allowed to dissociate into carbon monoxide and chlorine. It was found that the $COCl_2$ was 9% dissociated at equilibrium.
K_c for the process $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ at temperature, T, is

A 0.009
B 0.091
C 0.109
D 8.9×10^{-4}
E 8.1×10^{-4}

8. Excess solid ammonium hydrogen sulphide is heated in a sealed container to 295K until the equilibrium $NH_4HS(s) \rightleftharpoons H_2S(g) + NH_3(g)$ is established. The total pressure at equilibrium is 0.53 atm. K_p for the system is

A 0.265
B 0.28
C 0.070
D 1.06
E 0.079

9. According to the Bronsted-Lowry definition, an **acid** is a substance which donates a
A hydrogen atom.
B hydrogen ion.
C hydrogen molecule.
D hydride ion.
E hydroxide ion.

10. Which does NOT constitute an acid/base conjugate pair?
A H_2SO_4/ HSO_4^-
B HNO_3/HNO_2
C NH_4^+/ NH_3
D H_3O^+/ H_2O
E HNO_2/ NO_2^-

11. The $[OH^-]$ in $2x10^{-4}$ M hydrochloric acid is, in mol dm^{-3}, closest to

A $2x10^{-4}$
B $1x10^{-4}$
C $5x10^{-11}$
D 3.7
E 10.3

12. The acidity constant for an acid, HA, is 2.5×10^{-6}. The pK_b of its conjugate base is
A 5.6
B 8.4
C 1.79×10^{-5}
D 1.0×10^{-14}
E 14

13. Which salt would be expected to produce a solution with the **lowest** pH? Assume all solutions have the same molar concentration.
A KNO_3
B $Mg(NO_3)_2$
C $Al(NO_3)_3$
D $Ca(NO_3)_2$
E $Ba(NO_3)_2$

14. Which statement is usually true of an acid/base indicator?
A It is neither an acid nor a base.
B It always changes colour at pH 7.
C It always changes colour at a pH above 7.
D It always changes colour at a pH below 7.
E It is at the mid point of its colour change when pH = pK of the indicator.

Questions 15 and 16.

A 0.20 M solution of a weak monobasic acid is 5% dissociated at 298K.

15. The pH of the acid solution is closest to
A 0.01
B 0.20
C 0.70
D 1.0
E 2.0

16. The pK_a of the acid is closest to
A 3.3
B 0.70
C 2.0
D 0.20
E 5.25

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17. Which set shows the substances in order of **increasing** acid strength?
A HF, HBr, HCl.
B H_2SO_4, H_2SO_3, HSO_4^-.
C $HClO_4$, $HClO_3$, $HClO_2$.
D HF, H_2O, NH_3.
E CH_2FCOOH,CH_3COOH, $CH_2ClCOOH$,

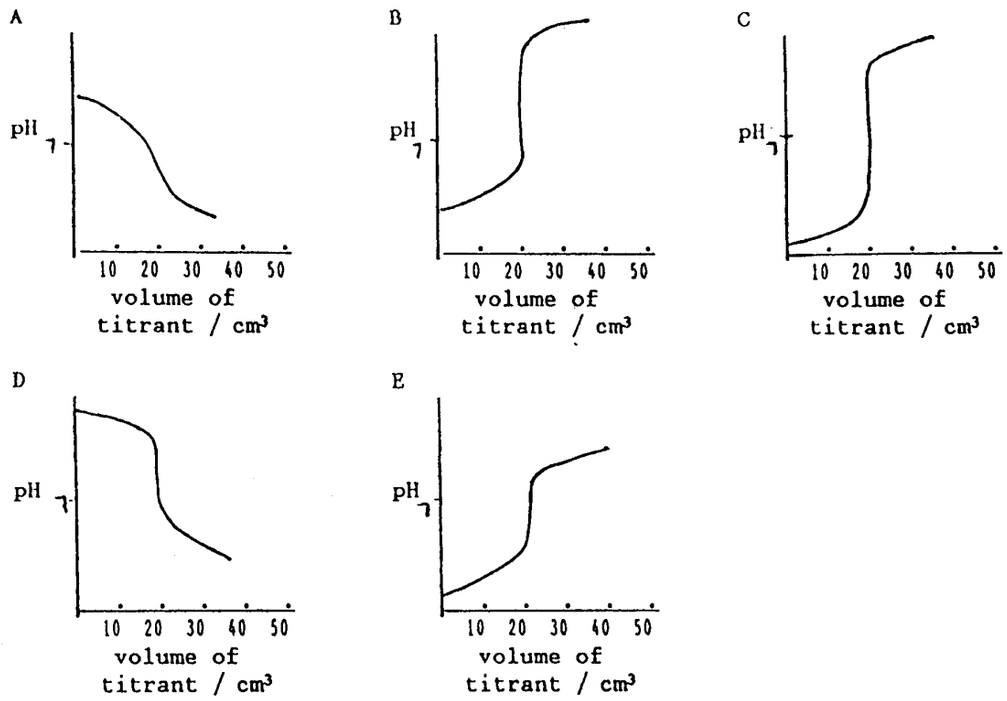
Questions 18 to 23 refer to the following solutions all at a concentration of $1x10^{-3}$ M

A $HClO_4$
B NaOCl
C $FeCl_3$
D NaCl
E NaOH

Select from A to E,

18. The solution which would have the lowest pH.
19. The solution which would have the highest pH
20. The solution which would have a pH closest to 3.
21. The solution which would have a pH closest to 7.
22. The solution which would have a pH between 3 and 7.
23. The solution which would have a pH between 7 and 11.

Questions 24 – 28 refer to the diagrams A to E which represent titration curves for the reaction between various acids and bases.



Choose, from A to E, the curve which best represents

24. the titration of 20 cm^3 of 0.1M HCl with 0.1M NaOH
25. the titration of 20 cm^3 of 0.1M HCl with 0.1M NH_3
26. the titration of 20 cm^3 of 0.1M CH_3COOH with 0.1M NaOH
27. the titration of 20 cm^3 of 0.1M NH_3 with 0.1M CH_3COOH
28. the titration of 20 cm^3 of 0.1M NaOH with 0.1M CH_3COOH

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29. A saturated solution of silver phosphate(Ag_3PO_4) contains $1.5x10^{-5}$ mol dm^{-3} Ag^+ ions. The solubility product of this compound is

A $(1.5x10^{-5})^4$
B $(4.5x10^{-5})^3 (1.5x10^{-5})$
C $(4.5x10^{-5})^3 + (1.5x10^{-5})$
D $4(1.5x10^{-5})$
E $4(1.5x10^{-5})^3$

30. In which compound does oxygen carry an oxidation number of +2 ?

A H_2O
B H_2O_2
C F_2O
D Na_2O
E CO_2

Questions 31 and 32 concern the following reactions:

A $KI + 3HOCl \rightarrow KIO_3 + 3HCl$
B $Fe + 2H_2SO_4 \rightarrow FeSO_4 + 2H_2$
C $SO_2 + H_2O \rightarrow H_2SO_3$
D $3S + 6NaOH \rightarrow 2Na_2S + Na_2SO_3 + 3H_2O$
E $XeF_2 + 2Cl^- \rightarrow Xe + 2F^- + Cl_2$

31. Which is NOT a redox reaction?

32. Which is a disproportionation reaction?

SECTION B: Answer **ALL** questions in the spaces provided on the question paper.

Use the following information where appropriate:
$R = 8.31\ J\ mol^{-1}\ K^{-1} = 0.082\ atm\ dm^3\ mol^{-1}\ K^{-1}$
$K_w = 1 \times 10^{-14}$

1. Benzene diazonium chloride, $C_6H_5N_2Cl$, in acidic solution is stable below 5^0C but rapidly hydrolyses in a first order reaction when heated to 50^0C.
$C_6H_5N_2Cl\ (aq) + H_2O\ (l) \rightarrow C_6H_5OH\ (aq) + HCl\ (aq) + N_2\ (g)$.

The decomposition of hydrogen peroxide is also a first order reaction
$2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$.

At 50^0C it is much slower than the hydrolysis of benzene diazonium chloride of the same concentration.

a] Write the rate equation for the decomposition of hydrogen peroxide.[1 mark]]

b] Comment on the **relative** values of the activation energies and the rate constants for the reactions above. [2 marks]

Activation energies:

Rate constants:

c] How does the value of the activation energy for the hydrolysis of benzene diazonium chloride at 50^0C compare to its value below 5^0C? [1 mark]

d] Explain, in terms of the collision theory, why the hydrolysis of benzene diazonium chloride is much faster at 50^0C than below 5^0C. [3 marks]

e] The decomposition of hydrogen peroxide is catalysed by iodide ions.
Explain how a catalyst is able to speed up the rate of a reaction. [2 marks]

2. Ammonia is manufactured by passing hot nitrogen and hydrogen at high pressure over a catalyst containing iron.

In an experiment, 9.0 moles of nitrogen and 27 moles of hydrogen were put into an iron vessel of volume 10.0 dm^3. This mixture was heated to 250^0C and allowed to reach equilibrium. It was found that two thirds of the reactants were converted to ammonia.

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ $\Delta H = -92.4\ kJ\ mol^{-1}$

a] Give the expression for K_c. [1mark]

b] Calculate the value of K_c at 250^0C. [3 marks]

c] Calculate the value of K_p at 250^0C. [2 marks]

d]] State the effect, if any, of an increase in temperature on the value of the **equilibrium constant**, K_c, giving a reason. [2marks]

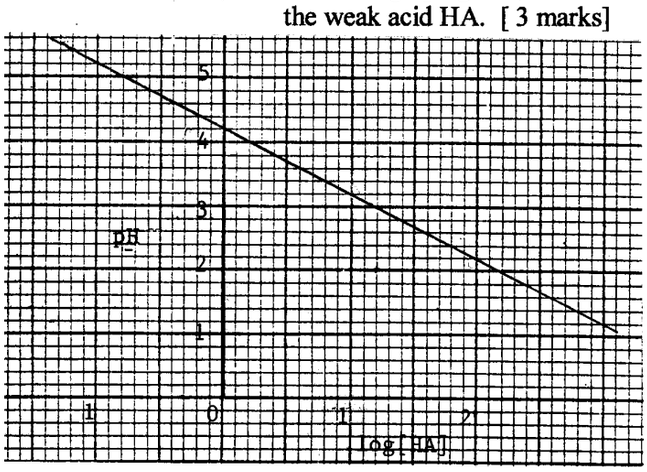
e] State the effect, if any, of an increase in pressure, by the addition of an inert gas, on the **equilibrium position**, giving a reason. [2 marks]

3. a] i) Write an expression for the equilibrium constant, K_a, for a weak monoprotic acid HA.[1 mark]

ii) Use this expression to derive the relationship

pH = ½ pK_a - ½ log [HA] for the acid. [2 marks]

iii) From the graph given, calculate the value of the acidity constant , K_a, for the weak acid HA. [3 marks]



4. Use the following information wherever necessary.

$K_w = 1 \times 10^{-14}$
$K_a(NH_4^+) = 6.3 \times 10^{-10}$

a] 25.0 cm^3 of 0.20 M NH_3 solution was titrated with 0.20M HCl solution. The table shows the pH of the resulting mixtures as various volumes of the acid were added to the base.

Volume of acid added/cm^3	pH
0.0	
5.0	9.8
10.0	
25.0	
30.0	1.7
35.0	

Complete the table. **Show your working** in the spaces provided below. [12 marks]

Volume of acid added: 0.00 cm^3

Volume of acid added: 10.0cm^3

Volume of acid added: 25.0cm^3

Volume of acid added: 35.0cm^3

b] i) From the table given, choose the most suitable indicator for this titration.

Indicator	pH range	Colour at lower pH	Colour at higher pH
Thymol blue	1.2 –2.8	Red	Yellow
Thymol blue	8.0 – 9.6	Yellow	Blue
Methyl orange	3.5 – 4.5	Red	Yellow
Methyl red	4.4 - 6.3	Red	Yellow
Bromothymol blue	6.0 – 7.6	Yellow	Blue

The most suitable indicator is ..... [1 mark]

ii) What colour **change** would you expect to see at the end point of the titration? [1 mark]

5. For each pair of substances given, underline the substance which will produce a solution of lower pH , assuming all solutions are at a concentration of 0.10 M. In each case give a reason for your answer, with equations and/ or Lewis structures to support your answer. [3 marks each]

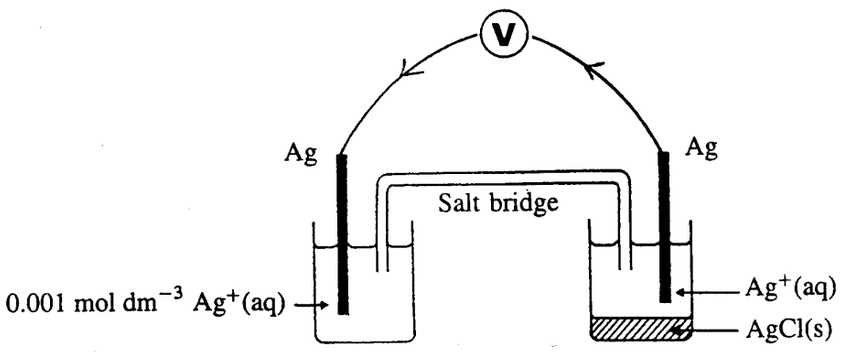
a] $Al_2(SO_4)_3$ and Na_2SO_4.

b] NaCl and NaOCl.

c] HNO_2 and HNO_3

d] HF and HCl.

6. The electrochemical cell shown below can be used to measure the solubility of silver chloride in water. The solution in the right hand half cell stands over a small amount of solid silver chloride.
The arrows show the direction of flow of electrons in the external circuit.



The potential of a silver ion/silver electrode is given by the Nernst equation

$$E_{Ag+/Ag} = E^0_{Ag+/Ag} - 0.059 \frac{1}{\log[Ag^+]} \quad \log \frac{1}{[Ag^+]}$$

The standard electrode potential for the Ag^+/Ag pair is +0.80 V, and the potential of the cell shown is 0.11V.

a] Label the negative electrode in the diagram. [1 mark]

b] Find the potential of the left hand half cell. [2 marks]

c] Find the potential of the right hand half cell, and hence find the solubility of silver chloride in mol dm^{-3} [3 marks]

d] Find the solubility product of silver chloride [2 marks]

e] Why is it important to have a small amount of solid silver chloride in the right hand beaker? [1 mark]

f] Salt bridges are usually made from solutions or gels containing potassium nitrate or potassium chloride. State which you would choose for this cell, and explain why. [2 marks]

g] Write a cell notation to represent the above cell. [1 mark]

7. a] Copper metal reacts with dilute nitric(V) acid to produce copper(11)nitrate and nitrogen(11)oxide.
Derive a balanced **ionic** equation for this reaction. [3 marks]

b] Solid bismuth oxide (Bi_2O_3) reacts with sodium chlorite(1),(NaOCl), in a basic medium to produce sodium bismuthate($NaBiO_3$) and sodium chloride.
Derive a balanced **ionic** equation for this reaction. [3 marks]

END OF EXAMINATION